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Headspace Solid Phase Microextraction 방법에 의한 HANs 분석에 관한 연구

Analysis of Haloacetonitriles in Drinking Water Using Headspace-SPME Technique with GC-MS

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Abstract

In many drinking water treatment plants, chlorination process is one of the main techniques used for the disinfection of water. This disinfecting treatment leads to the formation of disinfection by-products (DBPs) such as haloacetonitriles (HANs), trihalomethanes (THMs), haloacetic acids (HAAs). In this study, headspace-solid phase microextraction (HS- SPME) technique was applied for the analysis of HANs in drinking water. The effects of experimental parameters such as selection of SPME fiber, the addition of salts, magnetic stirring, extraction temperature, extraction time and desorption time on the analysis were investigated. Analytical parameters such as linearity, repeatability and detection limits were also evaluated.

The 50/30μm-divinylbenzene/carboxen/polydimethylsiloxane fiber, extraction time of 30 minutes, extraction temperature of 20°C and desorption time of 1 minute at 260°C were the optimal experimental conditions for the analysis of HANs. The correlation coefficients (r^2) for HANs was 0.9979~0.9991, respectively. The relative standard deviations (%RSD) for HANs was 2.3~7.6%, respectively. Detection limits (LDs) for HANs was 0.01~0.5μg/L, respectively.

Key words: HANs, HS-SPME, Drinking water analysis
주제어: HANs, HS-SPME, 먹는물분석방법

1. Introduction

Chlorination is an important disinfection method applied to drinking water supplies in order to prevent waterborne diseases. Chlorination inactivates pathogenic microorganisms and oxidizes many organic molecules to carbon dioxide. In the treatment of surface waters con-

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taining humic substances, however, it also produces chlorinated by-product and incompletely oxidized compounds that are potential toxins (Aiessman & Hammer, 1998).

Chlorine has traditionally been a preferred disinfecting agent because of its proven effectiveness and its being relatively inexpensive (Rodriguez & Serodes, 2001). Chlorination was reported to form haloacetonitriles (HANs) as a result of chlorination of natural water (Bull & Kopfler, 1991). The formation of HANs in drinking water results from the reaction of chlorine with naturally occurring organic matters, principally humic acid and fulvic acid.

1.1. Health effects

The haloacetonitriles (HANs) include chloroacetonitrile (CAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN). These haloacetonitriles have limited commercial use, but are produced during chlorination of water containing organic matter.

Subchronic effects of haloacetonitriles (in corn oil) have been investigated using rats. Doses of 65mg/kg of DCAN and DBAN for 90 days produced decreased weight gains, decreased organ weights and organ-to-body weight ratios of the liver, spleen, thymus, lungs, and kidneys. A decrease in blood cholesterol levels was also noted. CAN, DCAN, and TCAN were all fetotoxic (decreased offspring weight and postnatal growth) when a dose of 55mg/kg was administered to pregnant rats over 90 days. Studies on the mutagenicity of DBAN, BCAN, DCAN, and TCAN were positive in sister chromatid exchange and/or bacterial/microsome assays. Both DCAN and BCAN were shown to be mutagenic in Salmonella. In cultured human lymphoblasts, DNA strand breaks were produced by TCAN, BCAN, DBAN, and DCAN. Administration of TCAN and BCAN by gavage to mice at doses of 10mg/kg produced a significant increase in the number of benign lung tumors, and dermal application caused skin cancer in mice. When tested for cancer-initiating activity, DBAN, DCAN, TCAN and BCAN were all founded to be negative (US-EPA, 1991a). No EPA standards or goals have been proposed. Korea drinking water quality standard for TCAN, DCAN and DBAN are 4, 90 and 100μg/L, respectively.

1.2. Analytical methods

A number of analytical methods have been reported for the analysis of HANs and other volatile organic compounds in water such as liquid-liquid extraction, static headspace technique, dynamic headspace technique (Purge & trap) and solid-phase microextraction technique (van Langenhove, 1999; Kuran & Sojak 1996).

The liquid-liquid extraction method has some practical disadvantages of which the contamination risk from the solvent is the most potent. An attractive technique is the direct aqueous injection but it has problems with column stability and critical temperatures for column and injector. A comparison of a static headspace method with a purge and trap method of some chlorinated hydrocarbons showed similar results (Dietz & Singley, 1979). The purge and trap method is, however, more time-consuming. Headspace method is relatively less sensitivity compared with liquid-liquid extraction (Castello et al., 1986; European Standard EN ISI10301, 1997) As a result, static headspace is suitable for the analysis of samples with high contents of volatiles (Kuivinen & Johnsson, 1999).

Two basic types of extractions can be performed using SPME: direct and headspace extraction. In the direct extraction mode (SPME), the coated fiber is inserted into the sample medium and the analytes are transported directly to the extraction phase. To facilitate rapid extraction, some level of agitation is required to enhance transport of the analytes from the bulk of the solution to the vicinity of the fiber. For gaseous samples, natural convection and diffusion in the medium is sufficient to facilitate rapid equilibration. For aqueous matrices, more efficient agitation techniques, such as fast sample flow, rapid fiber or vial movement, stirring, or sonication are required. These actions are undertaken to reduce the effect caused by the depletion zone, which occurs close to the fiber as a result of fluid shielding and slow diffusion of analytes in liquid media.

Table 1. Operation conditions for GC-MS (HANs)

Class	Conditions	
Carrier gas	helium, 1ml/min	
Split ratio	1 : 1	
Inlet liner	0.75mmID (SPME injection sleeve)	
Injector temp.	260°C	
Oven	40°C for 3 min, 5°C /min to 80°C, 10°C /min to 150°C, 25°C/min to 250°C and held 2 min (total time 24 min)	
Solvent delay	5.5 min	
Interface temp.	250°C	
Mass (Source)	Mode EI positive, SIR mode	
	Electron energy	70eV
	Emission	200μV
	Temperature	200°C
	Multiplier	500V
	Reference gas	heptacosa
	Tune ion	69, 131, 219, 414

In the headspace mode (headspace-SPME), the analytes need to be transported through a layer of air before they can reach the coating. This approach serves primarily to protect the fiber coating from damage by high molecular-weight species and other non-volatiles present in the liquid sample matrix, such as humic materials or proteins. This headspace mode also allows modification of the matrix, such as a change of the pH, without damaging the fiber. Amounts of analyte extracted into the coating from the same vial at equilibrium using direct and headspace sampling are identical, as long as sample and gaseous headspace volumes are the same.

This is a result of the fact that the equilibrium concentration is independent of fiber location in the sample/headspace system. If the above condition is not satisfied, a significant sensitivity difference between the direct and headspace approaches exists only for very volatile analytes. The choice of sampling mode has a significant impact on extraction kinetics. When the fiber coating is in the headspace, the analytes are removed from the headspace first, followed by indirect extraction from the matrix. Therefore, volatile analytes are extracted faster than semi-volatile components since they are at a higher concentration in the headspace, which contributes to faster mass transport rates through the headspace.

Temperature has a significant effect on the kinetics of the process, by determining the vapor pressure of analytes. In fact, the equilibrium times for volatile components are shorter in the headspace SPME mode than for direct extraction under similar agitation conditions. This outcome occurs as a result of two factors: a substantial portion of analyte is in the headspace prior to extraction, and diffusion coefficients in the gas phase are typically four orders of magnitude larger than in liquid media. Since the concentration of semi-volatile components in the gas phase at room temperature is small, however, mass transfer rates are substantially lower and result in longer extraction times for such species. The situation can be improved by using of even more efficient agitation techniques, such as sonication, further reducing the extraction time. The other option is to increase the temperature; this decreases the amount extracted at equilibrium, but it may be acceptable if target limits of detection can still be attained. It is fast, sensitive, inexpensive, portable and solvent-free. No special sample work-up is required and sampling times are also short. The development of an internally cooled SPME device to achieve quantitative extraction for VOCs from gas, water and soil in combination with simultaneous heating of the sample was recently reported (Mester et al., 2001).

The aim of this study was to develop the rapid and simple method for HANs analysis in drinking water by head-

space SPME and then apply this technique for an investigation program concerning the HANs concentration in Seongnam (Kyonggi province) drinking water.

2. Experimental

2.1. GC-MS system and conditions

Separations were carried out on a Platform mass spectrometer (Micromass, Britain UK) equipped with Agilent 6890 gas chromatography. The analytical column was HP-5MS (60m × 0.25mmID, 0.25μm film thickness, J&W Scientific). The detailed operating conditions for GC-MS are shown in **Table 1**.

For quantification, characteristic ions of the spectrum obtained for haloacetonitriles were selected: 108m/z for trichloroacetonitrile, 74m/z for dichloroacetonitrile and bromochloroacetonitrile, 118/79m/z for dibromoacetonitrile.

2.2. Reagents

2.2.1. Reagent water

Standards and blanks were prepared from double distilled water (using a Milli-Q plus system from millipore, France) which was boiled for 1 hour in a large beaker.

2.2.2. Standard solutions

After opening vials or tubes containing standards or samples, they must be sealed as quickly as possible to avoid evaporation or contamination. Stock solutions of trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile containing each compound at 0.1mg/ml acetone were purchased from ChemService. Intermediate standard solutions at 2, 0.2, 0.02mg/L MeOH were obtained by the dilution of stock standard solution with MeOH (EM science, USA). The working standard solutions in the range of 0.05~20 μg/L aqueous (n = 9) were diluted from 2, 0.2, 0.02mg/L MeOH directly in 50ml vials.

Appropriate reagent water volume was 40ml in each vials (headspace volume 20ml). The standard solutions and samples were added into the internal standard (i.s., spiked at a level of 1μg/L of 1.2.3-trichloropropane (1.2.3-TCP, Supelco)) and 10g of sodium chloride (baked for 4 hrs at 450°C) was also added into the solution.

2.3. Sample collection

Water samples were collected in test tubes. The dechlorination agent (L-ascorbic acid, Junsei), as neat material, was first added into test tubes, 10mg for 10ml sample (Norin & Renberg, 1980). Before sampling, the tap was allowed to run for 3 minutes after the test tubes were carefully and completely filled. The sample were analyzed directly or stored up to a maximum of 3 days at 4°C.

2.4. Procedure for HS-SPME on calibrates and samples

SPME extraction was performed using a Supelco no. 57328-U manual solid-phase microextraction fiber assembly fitted with 50/30μm Divinylbenzene/carboxen/polydimethylsiloxane (50/30-DVB/CAR/PDMS) fiber. The fiber was equilibrated at 270°C for 1 hr prior to use and blank desorption was performed.

Samples (40ml) were transferred into vials (50ml, Supelco) which contained internal standard (1.2.3-TCP: 1 μg/L) and 10 g sodium chloride salt. The syringe assembly unit with the fiber was lowered into the vial with the fiber suspended in the headspace above the liquid layer of the samples at 20°C, and then samples were stirred at maximal speed without vortex using magnetic bar. Extraction time of 30 minutes was selected and the fiber was immediately retracted back into the needle and transferred without delay (less than 10 sec) to the injection port of gas chromatography. A desorption and conditioning times of 1 minute was adopted and the desorption temperature was 260°C.

The actual depth of the SPME needle in the injection port liner was controlled. Quantification of the four analytes was performed using the peak area ratios of the analyte relative to the internal standard (1.2.3-TCP, 1μg/L) based on multi-level calibration from 0.05 to 20μg/L (n = 9). Each standard was analyzed in duplicate.

The concentrations of analytes were automatically cal-

culated by relating to created calibration curves, where the peak area relationships (sample/i.s.) were plotted as a function of concentration (sample/i.s.).

3. Results and Discussion

3.1. Selection of SPME fibers

The efficiency of the extraction process is dependent on the analyte distribution constant between the coating and the sample matrix. This characteristic parameter describes properties of a coating and its selectivity toward the analyte versus other matrix components.

The SPME theory dictates that analytes in headspace are transferred into the phase coating of the fused silica fiber; equilibrium process was finally established between the concentration of the analytes in headspace and the concentration of analytes in the phase coating. The choice of an appropriate coating is essential for the establishment of a headspace SPME method and it is dependent on the chemical nature of the target analytes (Cancho et al., 2001).

In this study four types of fibers, 100μm polydimethylsiloxane (100-PDMS), 85μm polyacrylate (85-PA), 65μm polydimethylsiloxane/divinylbenzene (65-PDMS/DVB) and 50/30μm divinylbenzene/carboxen/polydimethylsiloxane (50/30-DVB/CAR/PDMS) were used to select the appropriate fiber for the analysis. New fibers were conditioned, following the manufacturer's recommendations.

Water samples (40ml spiked at a level of 20μg/L of HANs and 1μg/L of 1.2.3-TCP (i.s.)) were analyzed in duplicate with each fiber. The extraction time was 30 minutes at 20°C and desorption time was 1 minute at 260°C for all fibers.

In order to evaluate the extraction efficiency, the peak areas obtained for each HANs with the different fibers are shown in **Fig. 1**.

Extraction efficiencies for the HANs were increased according to the following order; 100-PDMS < 85-PA < 65-PDMS/DVB< 50/30-DVB/CAR/PDMS. The 50/30-DVB/CAR/PDMS fiber was the best coating due to its high capacity to extract these compounds. Compared to the 100-PDMS fiber (manufacturer's recommendation of VOC analysis), the relative response of the 50/30-DVB/CAR/PDMS fiber was 7, 24, 18 and 12 times greater for TCAN, DCAN, BCAN and DBAN, respectively.

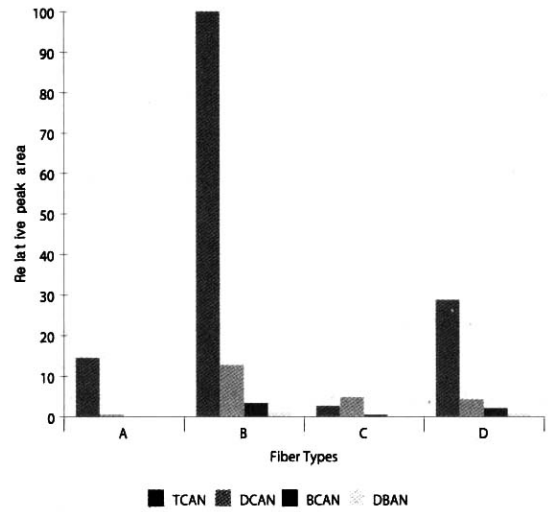

Fig. 1. Extraction efficiency of various fibers: extraction time of 30min at 20°C, desorption time of 1min at 260°C, HANs: 20μ/L, n = 2.
(A) 100-PDMS (B) 50/30-DVB/CAR/PDMS
(C) 85-PA (D) 65-PDMS/DVB

The polydimethylsiloxane (PDMS) fiber (a non-polar phase) is not the best coating due to its low capacity to extract these compounds. Property of the mixed divinylbenzene/carboxen/polydi-methylsiloxane (DVB/CAR/PDMS) fiber was different from that of PDMS due to the porous carbon adsorbent (Carboxen). This modifies the selectivity toward polar compounds and thus improves the extraction efficiency.

The 50/30μm-divinylbenzene/carboxen/polydimethylsiloxane fiber is suitable for the extraction of HANs with a relatively high efficiency due to the increase in the surface area of fiber and the suitable polarity.

3.2. Effect of the addition of salt and magnetic stirring

Addition of salts may result in the change of the vapor

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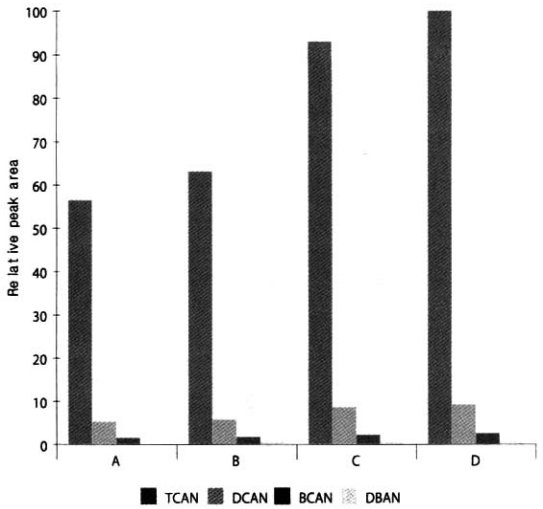

Fig. 2. Effect of the addition of salt and magnetic stirring on extraction: extraction time of 30 min at 20°C, desorption time of 1 min at 260°C, HANs: 20μg/L, n = 2..
(A) Static (B) Stirred (C) Static & Salts (D) Stirred & Salts

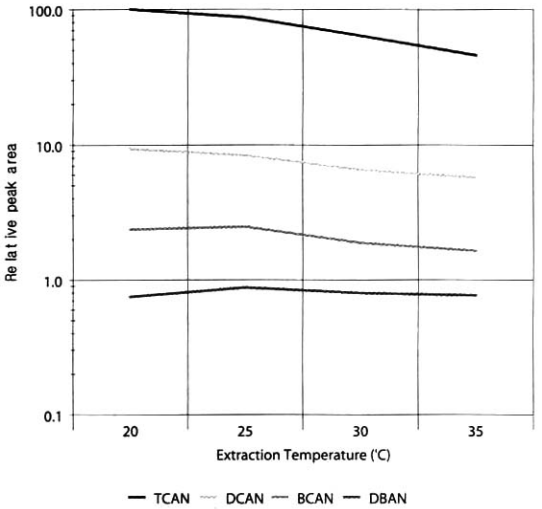

Fig. 3. Effect of extraction temperature on extraction: extraction time of 30 min, desorption time of 1 min at 260°C, HANs: 20μg/L, n = 2.

and partial pressure, solubility, thermal conductivity, density, surface tension, etc. of an analytes. These changes, if they occur, will result in the variation of the vapor/liquid equilibrium system (Banal et al., 1999).

Two techniques that have been used to improve performance (analyte recovery) in HS-SPME are sample stirring and addition of salt. To facilitate rapid extraction, some level of agitation is required to enhance transport of the analytes from the bulk of the solution to the vicinity of the fiber.

For gaseous samples, natural convection and diffusion in the medium is sufficient to facilitate rapid equilibration. For aqueous matrices, more efficient agitation techniques, such as fast sample flow, rapid fiber or vial movement, stirring, or sonication are required. These actions are undertaken to reduce the effect caused by the depletion zone, which occurs close to the fiber as a result of fluid shielding and slow diffusion of analytes in liquid media (Mester et al., 2001).

The highest recoveries of HANs was achieved with the agitation of samples and salts addition (**Fig. 2**). Compared to unsalted samples, relative recovery of salted samples was 1.6, 1.6, 1.4 and 1.3 times greater for TCAN, DCAN, BCAN and DBAN, respectively. When samples were stirred (with NaCl), recoveries of TCAN, DCAN, BCAN and DBAN were 1.8, 1.8, 1.7 and 1.6 times better than those at static conditions.

Salting out effect is used to decrease solubility of analytes of interest (including polar ones) in liquid samples. With HS-SPME, the addition of salt into the aqueous sample prior to the extraction process, increases of the ionic strength of the solution and overall SPME/sample partition coefficient (K_{fg}: a ratio of analyte concentration in stationary phase coated on fiber and in gaseous sample at equilibrium) were obtained. As a consequence, the diffusion of the analytes into the headspace is favored and extraction time for each analyte is reduced.

3.3. Effect of extraction temperature

In order to evaluate the extraction efficiency, the experiment was performed using 50/30-DVB/CAR/PDMS fiber and extraction temperature was increased from 20 to 35°C.

It can be seen from **Fig. 3** that TCAN and DCAN were yielded the higher extraction efficiencies at 20°C, whereas BCAN and DBAN, were yielded the higher extraction efficiencies at 25°C, respectively.

With HS-SPME, higher temperature may result in the increased vapor pressure of volatile analytes in the headspace owing on the temperature dependence of the Henry's constant. However, higher temperature may also have the negative effect of less favorable coating-headspace (air) partition coefficients (K_{fg}) (Zhang & Pawliszyn, 1993, 1995; Nilsson et al., 1995; Jia et al., 1998). Fiber internal cooling (extraction temperature) is useful in extraction from headspace (HS) when sample temperature must be increased to improve analytes transfer from a liquid sample to the headspace. To maintain high fiber coating/HS coefficients fiber temperature must be kept low. This approach ensures increased sensitivity due to increase in partition coefficients of HS/sample (increase temperature) and fiber/HS (decrease temperature) and hence increased ratio of analyte concentration in the fiber coating and the sample.

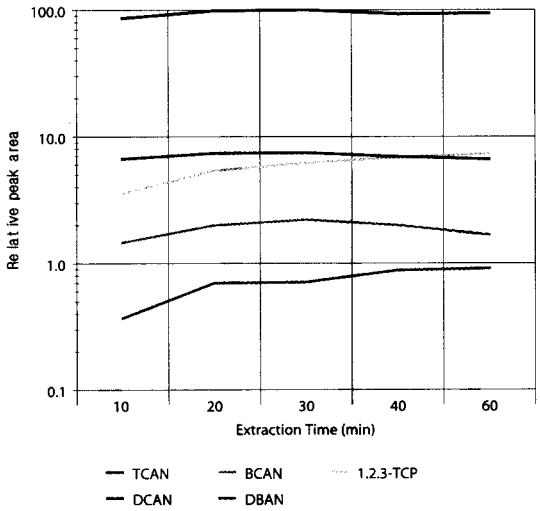

Fig. 4. Effect of extraction time from 10 to 60 min at 20°C on extraction: extraction temperature: 20°C, desorption time of 1 min at 260°C, HANs: 20μg/L, 1.2.3-TCP (i.s.): 1μg/L, n = 2.

3.4. Effect of extraction and desorption time

In order to evaluate extraction efficiency, the experiment was performed using 50/30-DVB/CAR/PDMS fiber and extraction time was increased from 10 to 60 minutes at 20°C. The peak areas obtained for each HANs with different extraction times are shown in **Fig. 4**.

According to the theoretical model, in a homogeneous mixed sample there is a diffusion of the analytes from the sample to the stationary phase, but there is no diffusion in the solution. The analyte concentration in the fiber increases rapidly at first, then more slowly until equilibrium is reached after a certain equilibrium time.

Acceptable equilibrium states (30min) were achieved for TCAN, DCAN, BCAN, DBAN and 1.2.3-TCP(i.s.). However, the equilibrium state was not reached until 60 minutes for DBAN and 1.2.3-TCP(i.s.), indicating that the diffusion of the analytes from the liquid phase into the headspace was important in the equilibration process. With extraction process, there is no need to achieve complete equilibrium concentrations if only the exposure time of the fiber is kept exactly constant.

In order to determine desorption time, the experiment was performed using 50/30-DVB/CAR/PDMS fiber and desorption time was increased from 0.5 to 2 minutes at 260°C (not printed). The desorption was completed for each compound after 0.5 minute at 260°C, indicating that the desorption of the analytes from the fiber was important in the desorption time and temperature.

Previous studies (Nilsson et al., 1995) on the effect of temperature on absorption of analytes showed that at lower temperatures the range of diffusion was slower and equilibration time was longer. Increasing the temperature decreases the distribution constants as absorption is generally on exothermic process and the amount of analyte absorbed onto the fiber decreased. In the headspace mode, the equilibrium was reached faster than an aqueous extraction, as the rate of diffusion is faster in the gaseous phase (Stack et al., 2000).

For this reason, the extraction time of 30 minutes at 20°C in the headspace mode and desorption time of 1 minutes at 260°C were selected for the linearity, repeatability and detection limits (LDs) studies.

3.5. Linearity, repeatability and detection limits

The linearity range of the HS-SPME method was evaluated by plotting the calibration curves of the area relative

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Table 2. Correlation coefficients (r^2) of linearity, repeatability and limits of detection at standard concentration range from 0.05 to 20μg/L.

Compound	R.T. (min)	STD Range	Linear (r^2)	%RSD 10 (n = 5)	LDs (mg/L)
TCAN	6.46	0.05~20	0.9984	9.69 (4.2)	0.01
DCAN	7.32	0.5~20	0.9979	11.12 (7.6)	0.1
BCAN	10.16	0.5~20	0.9988	10.82 (3.7)	0.1
DBAN	13.31	1~20	0.9991	10.21 (2.3)	0.5

to the internal standard 1.2.3-trichloropropane versus the concentration of each analyte. Standard calibration curves were plotted for concentrations ranging from 0.05 to 20 μg/L (n = 9). The correlation coefficients (r^2) of linearity obtained for each compound are shown in **Table 2**.

The correlation coefficients (r^2) for TCAN, DCAN, BCAN and DBAN were 0.9984, 0.9979, 0.9988 and 0.9991 when analyte concentration ranges from 0.05 to 20 μg/L, respectively.

The sensitivity of the HS-SPME method was considered in terms of detection limits (LDs) which depend on the basis of the signal-to-noise ratio (s/n > 3). The average s/n of triplication at low concentration was used the LDs, under the experimental conditions, the detection limits (**Table 2**) were 0.01μg/L for TCAN, 0.1μg/L for DCAN and BCAN, and 0.5μg/L for DBAN.

The repeatability of HS-SPME was investigated by analyzing the fortified reagent water. The relative standard deviations (%RSD) for repeatability ranges 2.3~7.6 % at standard concentration of 10μg/L, indicating that HS-SPME was properly performed.

Previous studies (Lee et al., 2001) showed that the correlation coefficients (r), LOD and %RSD were 0.998~1.000, 0.25~0.5μg/L and 4.2~13.4 %, respectively, in liquid-liquid extraction method.

3.6. HANs concentrations in Seongnam drinking water

The method described has been used for HANs investigations of Seongnam (Kyonggi province, Korea) drinking water. Bok-Jeong (Seongnam) water treatment plants supply water to nearly 600 thousand peoples, treating 280,000m^3/day, and chlorination process is the only technique used for disinfection of drinking water. The sampling was performed at the terminal point for the distribution system in October 2003.

The range of DCAN concentrations was 1.47~4.44 μg/L. The other HANs were trace level or not detected. The highest DCAN concentration was recorded at tap-water 18, with a level of 4.44μg/L (Table 3). The average concentration was 2.51μg/L

The results of DCAN concentration was well within the Korea drinking water quality standard of 90μg/L. It can be concluded that HS-SPME technique has a great potential for the analysis of drinking water.

Table 3. HANs concentrations (μg/L) in Seongnam drinking water (October 2003).

Sample sites	TCAN	DCAN	BCAN	DBAN
water treat. plant	Tr	1.47	Tr	ND
Tap-water 1	Tr	3.30	Tr	ND
Tap-water 2	Tr	1.86	Tr	ND
Tap-water 3	Tr	1.82	Tr	ND
Tap-water 4	Tr	3.25	Tr	ND
Tap-water 5	Tr	2.34	Tr	ND
Tap-water 6	Tr	2.00	Tr	ND
Tap-water 7	Tr	2.64	Tr	ND
Tap-water 8	Tr	2.67	Tr	ND
Tap-water 9	Tr	3.74	Tr	ND
Tap-water 10	Tr	3.19	Tr	ND
Tap-water 11	Tr	1.69	Tr	ND
Tap-water 12	Tr	2.57	Tr	ND
Tap-water 13	Tr	2.33	Tr	ND
Tap-water 14	Tr	2.02	Tr	ND
Tap-water 15	Tr	1.88	Tr	ND
Tap-water 16	Tr	1.67	Tr	ND
Tap-water 17	Tr	2.85	Tr	ND
Tap-water 18	Tr	4.44	Tr	ND
Tap-water 19	Tr	2.54	Tr	ND
Average	Tr	2.51	Tr	ND

4. Conclusions

Headspace-solid phase microextraction (HS-SPME) technique was applied to determine haloacetonitriles (HANs) in drinking water. Experimental parameters such as selection of SPME fiber, magnetic stirring, salts addition, extraction temperature, extraction time and desorption time were studied. The 50/30μm Divinylbenzene/carboxen/polydimethylsiloxane fiber, extraction time of 30 minutes, extraction temperature of 20°C and desorption time of 1 minute at 260°C were the optimal experimental conditions for the analysis of haloacetonitriles.

The correlation coefficients (r^2) for TCAN, DCAN, BCAN and DBAN were 0.9984, 0.9979, 0.9988 and 0.9991, respectively. The relative standard deviations (%RSD) for HANs were 2.3~7.6% for concentration of 10μg/L (n = 5). Detection limits (LDs) were 0.01~0.5 μg/L.

It can be concluded that headspace solid-phase microextraction (HS-SPME) technique has a great potential for the analysis of haloacetonitriles (HANs) in drinking water.

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